ARB-OEHHA Status Report on AB 1900 Efforts

Presentation to the CPUC
Second Workshop for
Rulemaking 13-02-008
May 2, 2013

Overview

- AB 1900
- ARB-OEHHA Process
- Constituents in Biogas
- Exposure Scenarios for Residents and Workers
- Constituents of Concern
- Recommended Health Protective Levels for Constituents of Concern
- Recommended Risk Management Approach
  - Monitoring, Reporting, Recordkeeping
- Next Steps

AB 1900

- Requires CPUC to adopt standards by Dec 31, 2013 for biomethane injected into the common carrier pipeline that:
  - (1) protect public health
  - (2) ensure pipeline integrity and safety
- ARB to propose health based standards for constituents of concern in biomethane by May 15, 2013
  - In consultation with OEHHA, DTSC, CalRecycle, and Cal-EPA
  - ARB is also to provide recommendations on monitoring, testing, reporting, and recordkeeping requirements
  - CPUC to give "due deference" to ARB recommendations

AB 1900
ARB-OEHHA Tasks

- Compile list of constituents of concern in biogas (OEHHA)
- Determine health protective levels for constituents (OEHHA)
- Identify realistic exposure scenarios (ARB)
- Determine appropriate concentrations of constituents (ARB)
- Identify reasonable monitoring, testing, reporting, and recordkeeping requirements (ARB)
- Due May 15, 2013, with updates at least every five years

Process

- ARB-OEHHA develops recommended health based standards
  - Informal public process
  - Relying on existing sources of data
- CPUC to adopt standards through their regulatory process
  - CPUC give due deference to ARB/OEHHA recommendations
- Two public workshops under the CPUC process (includes today's meeting)

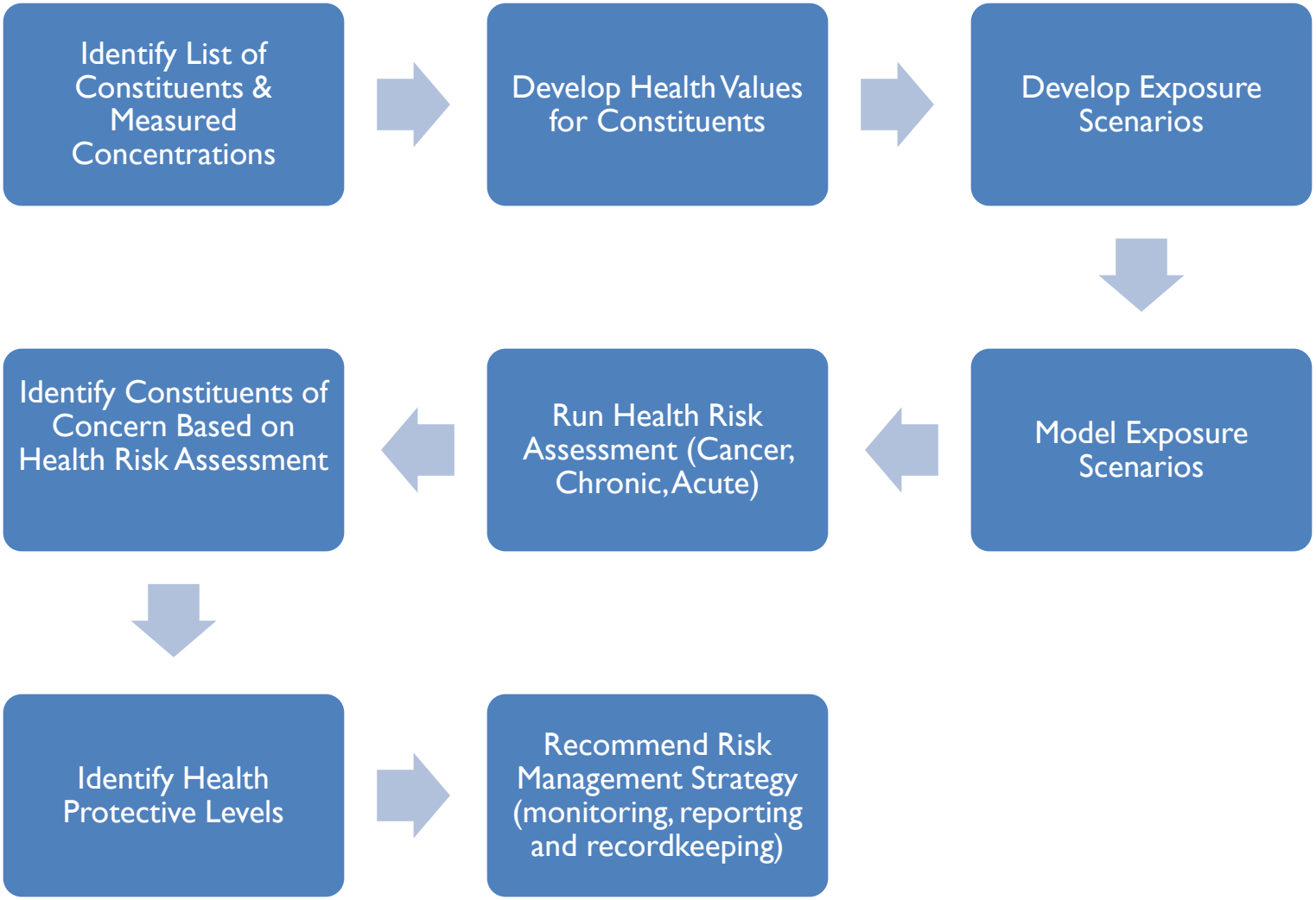
ARB-OEHHA Informal Public Process

- Two public meetings (April 10 & 25)
- Established Website
  - www.arb.ca.gov/energy/biogas/biogas.htm
  - Posted updates and staff presentations
- List Serve established for interested stakeholders
- Met with interested parties upon request
- Coordinated with other State agencies

Focus

- Biogas generated from larger sources with greatest potential for injection into the pipeline
  - Landfills, dairies, and POTW's (sewage treatment)
- Analyzed available data from both raw biogas and biomethane (upgraded biogas)
- Primary focus on directly emitted emissions
- Can address additional sources of biogas in AB 1900-mandated updates

Tasks Overview



List of Constituents

- Identified approximately 270 chemicals and chemical groups in biogas
  - All are at trace levels—total Non-Methane Organic Carbon (NMOC) ~ 0.1% of gas
- Many of these are likely biologic or chemical degradation products of biological materials
- Primary sources of data: Gas Technology Institute, LA County and Orange County Sanitation Districts, U.K. Landfill Study, and U.S. EPA

Identification of Health Values

- Used four main sources of toxicity data and risk values for risk evaluation:
  - OEHHA Reference Exposure Levels (RELs) for non-carcinogens, and Cancer Slope Factors for carcinogens
  - U.S. EPA Reference Concentrations and Cancer Slope Factors
  - ATSDR Minimal Risk Levels (MRLs)
  - Worker protection values from OSHA, NIOSH, or ACGIH
- Developed several screening values based on surrogate chemicals
- Identified risk-screening values for ~180 constituents, and defined surrogate screening values for ~25 additional chemicals and groups

Risk Evaluation

Health Risk Assessment

- Use emissions and mathematical model to estimate exposure concentrations
- Use OEHHA recommended health values and exposure assumptions to estimate:
  - Potential Cancer Risk
    - Evaluation of the potential for a chemical to cause cancer, expressed as number of excess cancers in a population of a million over a specified exposure duration
  - Acute and Chronic Hazard Quotient
    - The ratio between the exposure concentration and Reference Exposure Level for an individual compound

Exposure Scenarios Evaluated

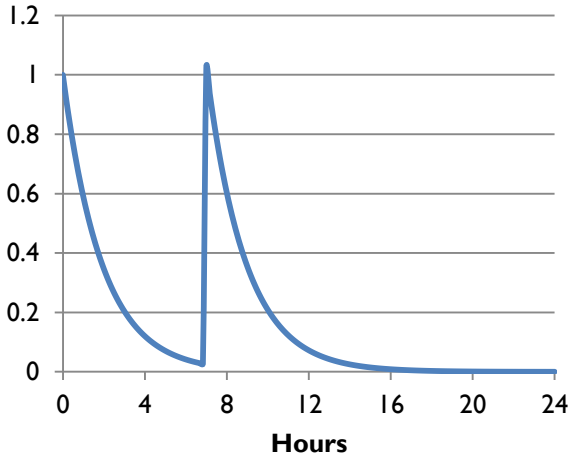
- Four Exposure Scenarios
  - Two Residential
    - Leak in a home
    - Stovetop pre-ignition phase
  - Two Worker
    - Losses at a biogas production facility
    - Utility worker service calls
- Four Gas Streams
  - Natural Gas, POTWs, Landfills, Dairy
- Conservative Assumptions
  - Assumed 100% biogas/biomethane in the pipeline
  - Used highest measured concentrations for constituents

Residential Exposure Scenario-Leak

- Residential Leak Scenario
  - Leak is 0.7% of the average household consumption
    - 0.003 m^3/hour
    - Below smell detection level
  - Assume 1-year exposure
- Indoor Box Model
  - Home Air Exchange Rate – 0.54
  - Home Size – 1,700 ft^2
  - Kitchen Size - 475 ft^2

Residential Exposure Scenario- Stovetop

- Stovetop Pre-Ignition Phase
  - 5 second pre-ignition phase
  - Two 2 hour cook periods per day (4 hours total)
  - Time decay analysis to determine emission factors
  - Assume 30-year exposure
- References
  - EPA – Introduction to Indoor Air Modeling
  - Risk Assessment of Biogas Exposure in Kitchens (France/UK)



Worker Exposure Scenario – Biogas Facility

- Production Facility Leak Scenario
  - Leak is 0.1% of the average biogas production
    - 0.89 m^3/hour
    - Below the smell detection level
  - Assume 25-year exposure
- Indoor Box Model
  - Production Facility Air Exchange Rate – 1.4
  - Biogas Production Facility Size – 2,500 ft^2
  - Biogas Production 750,000 ft^3 per day

Utility Worker Service Call Exposure Scenario

- Utility worker service calls to residences to check on appliance with gas leak (in kitchen)
- Exposure from gas leak at residences- 3 calls per day, 13 minutes per call
- Assume 25-year exposure
- Used same leak and inputs as residential leak scenario
  - Indoor Box Model
  - Leak rate of 0.003 m^3/hour
  - Below smell detection level
  - Home Air Exchange Rate – 0.54
  - Home Size – 1,700 ft^2
  - Kitchen Size - 475 ft^2

Dilution Values

Scenario	24 hour Average Dilution Factor	1-Hour Maximum Acute Dilution Factor
Residential Leak Scenario*	4.26E-05	1.28E-04
Residential Stovetop Scenario Factor	5.27E-06	4.81E-05
Biomethane Production Facility Worker Leak Exposure Scenario**	4.46E-04	4.46E-04
Utility Worker Service Call Exposure Scenario	2.76E-05	3.45E-06

*Residential leak scenario results in highest residential exposure concentrations

**Biomethane production facility worker leak exposure scenario results in highest worker exposure concentrations

Cancer Risk Calculations- Residential Leak Exposure Rate

- Potential residential cancer risk is highest for the residential leak scenario, compared to the residential stovetop scenario
- The equation for the residential leak exposure scenario is:

$$Exposure\ Rate\ \left(\frac{mg}{kg \cdot day}\right)$$

$$= C_r\ x\ DF_r\ x \left(\frac{1}{AT}\right) \sum_{i=1}^{4} IR_i\ x\ ED_i\ x\ SF_i\ x\ FAH_i$$

- Where
- C = Constituent concentration in biogas (highest measured values, mg/m^3)
- DF_r = Modeled dilution factor for the residential leak scenario (unitless)
- AT = Averaging time for exposures in cancer risk calculations (70 yr)

Cancer Risk Calculations- Residential Leak Exposure Rate

$$Exposure\ Rate\ \left(\frac{mg}{kg \cdot day}\right)$$

$$= C_r\ x\ DF_r\ x\ \left(\frac{1}{AT}\right) \sum_{i=1}^{4} IR_i\ x\ ED_i\ x\ SF_i\ x\ FAH_i$$

Age Category (yr)	IR_i = Inhalation rate (m^3/kg-d)	ED_i = Exposure duration (yr)	SF_i = Sensitivity factor (unitless)	FAH_i = Fraction of time at home (unitless)
3rd Trimester	0.361	0.3	10	0.85
0 < 2	1.09	2	10	0.85
2 < 16	0.745	14	3	0.72
16 < 30	0.335	14	1	0.73

ED_i is 1 year for residential leak scenario (using the most sensitive 0<2 yr age category)

Cancer Risk Calculations- Biomethane Worker Scenario

- Potential worker cancer risk is highest for the biomethane worker scenario, compared to the utility service call worker
- The equation for the worker exposure is:

$$Exposure\ Rate\ \left(\frac{mg}{kg \cdot day}\right)$$

$$= \frac{C\ x\ DF_w\ x\ IR_w\ x\ EF_w\ x\ ED_w}{AT}$$

- C = Constituent concentration in biogas (highest measured values, mg/m^3)
- DF_w = Modeled dilution factor for the biomethane worker scenario (unitless)
- IR_w = Worker 8-hour breathing rate (0.23 m^3/kg-8 hr day, 95%ile for moderate exertion)
- EF_w = Exposure frequency (5/7 d/d)
- ED_w = Duration of employment (25 yr; 95%ile value)
- AT = Averaging time in cancer risk calculations (70 yr)

Cancer Risk Calculations

- Lifetime potential cancer risk is the exposure rate multiplied by the cancer potency factor for that constituent:

$$Cancer\ Risk\ (chances) = Exposure\ Rate\left(\frac{mg}{kg \cdot day}\right) x\ Cancer\ Potency\ Factor\left(\frac{mg}{kg \cdot day}\right)^{-1}$$

Chronic Hazard Quotient Calculation

- Non-cancer risk is driven by chronic exposure, compared to acute exposure
- Residential leak scenario and biomethane worker scenario had highest calculated HQs
- The equation for non-cancer chronic exposure is:

$$Hazard\ Quotient = \left(\frac{C\ x\ DF_{w\ or\ r}}{Chronic\ NC\ REL}\right)$$

Where

- C = Constituent concentration in biogas (highest measured values, ug/m^3)
- $DF_{w\ or\ r}$ = Modeled 24 hour average dilution factor for the biomethane worker scenario or residential leak scenario (unitless)
- Chronic NC REL = chronic non-cancer reference exposure limit for the constituent (ug/m^3)

Identifying Constituents of Concern (CoC)

- CoC identified on a per-chemical basis
- Calculated non-cancer Hazard Quotients (HQs) and cancer risks for chemicals and groups
  - Used the highest modeled concentration
  - Used OEHHA methodology for calculations of exposure and risk
  - Focused on health effects of inhalation exposures

Constituents of Concern (cont)

- Criteria for identification of CoC
  - For chemicals with quantified risks, CoC are those with values greater than specified risk-thresholds
- CoC risk-thresholds for chemicals with quantified risks:
  - Residential: 0.01 for HQs and 1 in a million for cancer risks
  - Worker: 0.3 for HQs and 30 in a million for cancer risks

Results for Constituents of Concern

- Identified 12 CoC
  - All have quantified risk values
- 10 of the constituents were present in biogas (raw)
  - Constituents varied depending on biogas source
- 4 of the CoC were present at low levels in biomethane (upgraded biogas)
  - All non-cancer

List of Constituents of Concern in Biogas/Biomethane

- Arsenic*
- Vinyl Chloride*
- p-Dichlorobenzene*
- N-Nitroso-di-n-propylamine*
- Ethylbenzene*
- Hydrogen sulfide
- Antimony
- Alkyl thiols (mercaptans)
- Methacrolein
- Toluene
- Copper
- Lead

* Denotes the chemical is a carcinogen, constituents without * included due to chronic HQ

Biogas Source Specific Constituents of Concern

Constituent	Landfill	POTW	Dairy
Antimony	X		
Arsenic	X		
Copper	X		
p-Dichlorobenzene	X	X	
Ethylbenzene	X	X	X
Hydrogen Sulfide	X	X	X
Lead	X		
Methacrolein	X		
n-Nitroso-di-n-propylamine	X		X
Mercaptans (alkyl thiols)	X	X	X
Toluene	X	X	X
Vinyl Chloride	X	X	

OEHHA Recommended Health Protective Levels for Constituents of Concern

Constituent	OEHHA Health Protective Levels (mg/m^3)	OEHHA Health Protective Levels (ppm)
Vinyl Chloride*	0.84	0.33
Dichlorobenzenes (as p-Dichlorobenzene)*	5.7	0.95
n-Nitroso-di-n-propylamine*	0.033	0.0062
Ethylbenzene*	26	6.0
Arsenic*	0.019	0.0062
Hydrogen Sulfide**	30	22
Antimony**	0.60	0.12
Methacrolein**	1.10	0.38
Toluene**	900	240
Alkyl thiols (mercaptans)**	N/A	12
Copper**	0.060	0.023
Lead**	0.075	0.0089

Residential risk at one chance per million or Chronic HQ at 0.1
*Potential Cancer risk
**Chronic Non-cancer risk
The non-cancer health protective levels were constrained by the chronic HI

Risk Management Recommendation

- Relies on ARB and OEHHA's exposure modeling and risk analysis
- Similar to approach in ARB's Risk Management Guidelines for New and Modified Sources of Toxic Air Pollutants
  - Integrate risk levels into risk management decisions
  - Identify trigger levels and lower and upper action levels
  - Consider cancer and non-cancer risks
  - Ensure potential health risks are avoided

Recommended Cancer and Non-cancer Risk Levels and Actions

Risk Management Approach	Potential Cancer Risk (chances/10^6)	Non-cancer total hazard index (HI)	Action/Monitoring Frequency
Below Trigger Level	<1[a]	<0.1[a]	Annual Testing
Trigger Level (OEHHA Health Protective Level)	≥1[a]	≥0.1[a]	Quarterly Testing
Lower Action Level (LAL)	≥10[b]	≥1[b]	Quarterly Testing, Shut-off if 3rd test above LAL[c]
Upper Action Level	≥25[b]	≥5[b]	Immediate Shut-off

a For any single constituent. Approach modified HI from 1993 ARB Guidance from 0.2 to 0.1.
b Sum of all constituents of concern exceeding trigger level. Approach modified upper action level from 1993 ARB Guidance from 100 chances/million and HI of 10, to 25 chances/ million and HI of 5.
c Within a 12 month period.

Recommended Cancer and Non-cancer Risk Management Levels

Constituent of Concern	Risk Management Levels (Health Based Standards) mg/m³ (ppmv)		
	Trigger Level	Lower Action Level	Upper Action Level
Carcinogenic Constituents of Concern			
Arsenic	0.019 (0.0062)	0.19 (0.062)	0.48 (0.15)
p-Dichlorobenzene	5.7 (0.95)	57 (9.5)	140 (24)
Ethylbenzene	26 (6.0)	260 (60)	650 (150)
n-Nitroso-di-n-propylamine	0.033 (0.0061)	0.33 (0.061)	0.81 (0.15)
Vinyl Chloride	0.84 (0.33)	8.4 (3.3)	21 (8.3)
Non-carcinogenic Constituents of Concern (Chronic)			
Antimony	0.60 (0.12)	6.0 (1.2)	30 (6.1)
Copper	0.060 (0.02)	0.60 (0.23)	3.0 (1.2)
Hydrogen Sulfide*	30 (22)	300 (216)	1,500 (1,080)
Lead	0.075 (0.0089)	0.75 (0.089)	3.8 (0.44)
Methacrolein	1.1 (0.37)	11 (3.7)	53 (18)
Alkyl Thiols	N/A (12)	N/A (120)	N/A (610)
Toluene	900 (240)	9,000 (2,400)	45,000 (12,000)

Monitoring Recommendation

- Monitor for constituents based on sources of biogas
  - 12 for landfill, 6 for POTW's, 5 for dairy
  - In general-annual monitoring for any CoC that is below trigger level, quarterly for any CoC above trigger level*

* H_2S to be monitored continuously if of concern

Constituent	Landfill	POTW	Dairy
Antimony	X		
Arsenic	X		
Copper	X		
p-Dichlorobenzene	X	X	
Ethylbenzene	X	X	X
Hydrogen Sulfide	X	X	X
Lead	X		
Methacrolein	X		
n-Nitroso-di-n-propylamine	X		X
Mercaptans (alkyl thiols)	X	X	X
Toluene	X	X	X
Vinyl Chloride	X	X	

Recommendation for Pre-injection Start-up Testing

- Conduct tests for the constituents of concern for biogas source
- Two pre-injection tests over 2-4 weeks
- Utility and biogas producer agree on an approach to monitor performance of biogas treatment system
  - Natural gas tariffs may be good surrogate for demonstrating biogas treatment system is functioning properly
- If all constituents of concern for that biogas source below LAL then can inject into pipeline

Repeat of Pre-injection Start-up Testing

- Repeat of pre-injection start-up testing to be conducted when:
  - There is a change in the biogas cleanup equipment design
  - A new source of biogas is accepted
  - Biomethane production process has been shut-off due to any exceedance of the UAL or the third exceedance of the LAL in a 12 month period

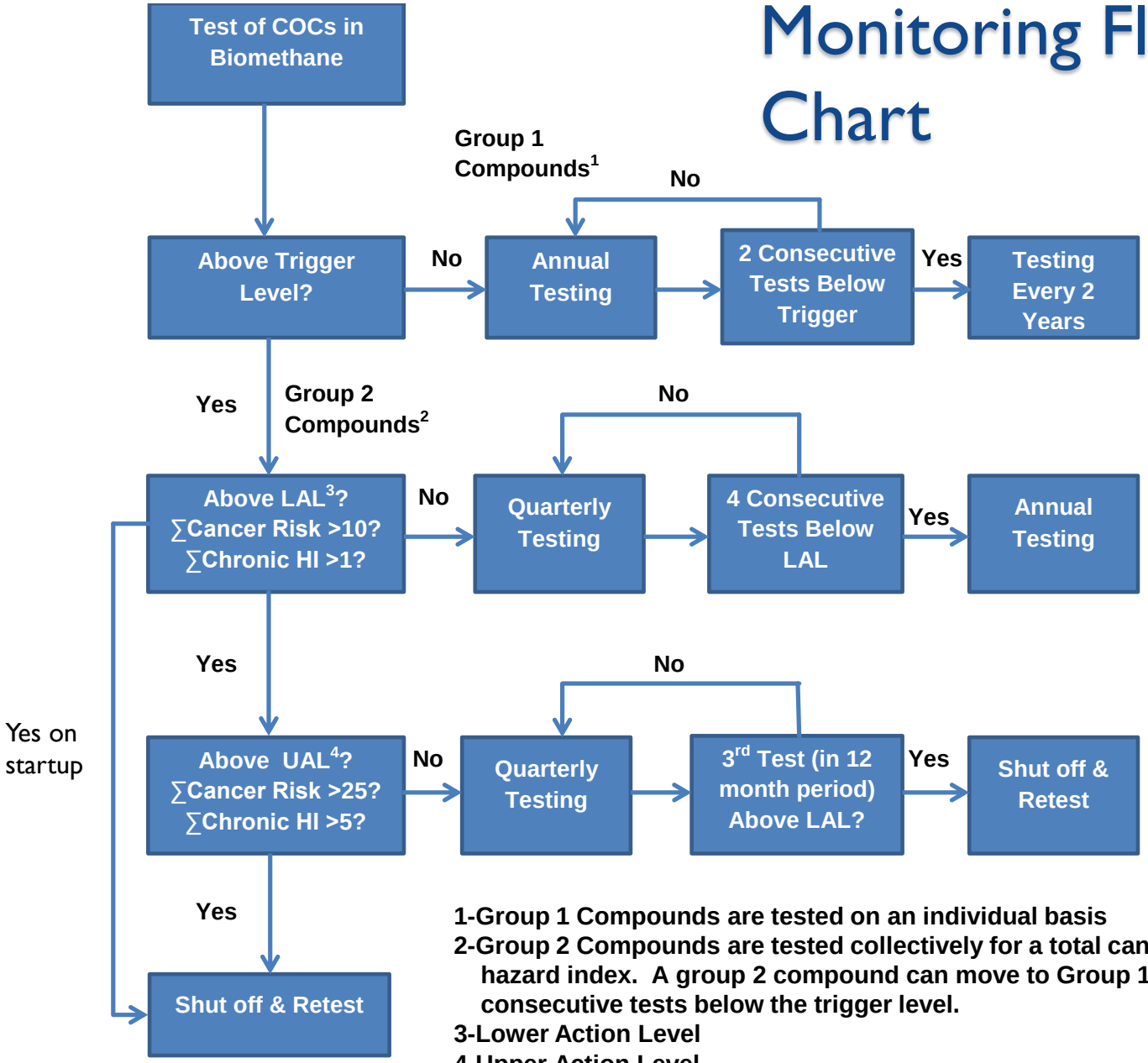
Periodic Testing of Constituents of Concern

- Trigger level is applied to an individual constituent
- For individual CoC not detected or below the trigger level during pre-injection start-up
  - Require annual monitoring
  - After two consecutive annual tests below the trigger level, monitoring can transition to every other year.

Periodic Testing of Constituents of Concern (cont)

- For CoC above the trigger level require quarterly monitoring
  - For an individual CoC
    - If 4 quarterly tests in 12 month period demonstrate CoC below trigger level, then constituent can go to annual testing
  - For group of CoC being monitored
    - LAL and UAL applied to combined risk for all CoC monitored
    - Shut-off if risk exceeds UAL, or LAL 3 times in12 months
    - If 4 consecutive tests demonstrate risk below LAL, then CoC can go to annual testing
    - ARB to provide web-based tool to calculate total risks based on measured concentrations of CoC

Monitoring Flow Chart



1-Group 1 Compounds are tested on an individual basis
2-Group 2 Compounds are tested collectively for a total cancer risk and hazard index. A group 2 compound can move to Group 1 after 4 consecutive tests below the trigger level.
3-Lower Action Level
4-Upper Action Level

Example

- POTW biomethane producer wants to inject into the common carrier pipeline
- Tests 6 constituents of concern twice
  - 4 constituents individually below trigger level
  - 2 above trigger level but below LAL
- Biomethane producer and utility agree on approach to monitor performance of biogas treatment system
- Injection can start
  - Four constituents tested annually; other two quarterly
  - Testing frequency may change in future based on periodic test results

Recommended Test Methods for CoC

Proposed CoCs	Approximate Levels	Risk Type	Recommended Test Method
Metals	**ppb**		
Lead	9 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Antimony	120 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Arsenic	6 ppb	Cancer Risk	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Copper	23 ppb	Chronic HQ	EPA Method 29 (AAS and/or ICP)/ EPA 200.8
Nitroso Compds	**ppb**		
n-Nitroso-di-n-propylamine	6 ppb	Cancer Risk	EPA 8270D (GC/MS)
Sulfur Compds	**ppm**		
Hydrogen Sulfide	22 ppm	Chronic HQ	ASTM D4084, D7165, D7493 (online monitoring), ASTM D5504, D6228 (lab)
Total Mercaptans (alkyl thiols)	12 ppm	Chronic HQ	ASTM D7165, D7493 (online monitoring), ASTM D5504, D6228
SVOCs	**ppm**		
Dichlorobenzenes (as p-Dichlorobenzene)	0.95 ppm	Cancer Risk	TO-15 (GC/MS)
VOCs	**ppb**		
Vinyl Chloride	330 ppb	Cancer Risk	TO-15 (GC/MS)
Methacrolein	380 ppb	Chronic HQ	TO-11A (Determination of Formaldehyde, Adsorbent Cartridge (HPLC))
Alkyl Benzenes	**ppm**		
Ethylbenzene	6 ppm	Cancer Risk	TO-15 (GC/MS)
Toluene	240 ppm	Chronic HQ	TO-15 (GC/MS)

Recommendations for Recordkeeping and Reporting

- Retain records of test results for 3 years
- Provide annual report to CPUC, ARB and OEHHA
  - All test data
  - Annual biomethane production rate
  - Monitoring parameters to ensure cleanup system operating effectively
  - Any shutdown event, reason and remedy
- If utility is testing entity, report to biomethane producer
  - Test results within 2 weeks, 24 hours for shutoff levels.
- If biomethane producer is testing entity, report to utility same information

Next Steps

- Submit report electronically to CPUC by May 15th, post on ARB website
- Provide technical support to CPUC during the regulatory process
  - Integrate risk management strategy with pipeline safety requirements
  - Integrate monitoring, recordkeeping and reporting requirements with current practices used to ensure pipeline safety requirements
  - Identify process for adding new biogas stream, adding/removing constituents of concern
- Evaluate areas for further investigations at the next AB 1900-mandated update